

# SECOND AND THIRD LAWS OF THERMODYNAMICS

## Structure

---

4.1	Introduction	4.3	The Second Law of Thermodynamics
	Expected Learning Outcomes		
4.2	Spontaneity	4.4	The Gibbs Energy
	Spontaneous and Non-Spontaneous Processes	4.5	The Third Law of Thermodynamics
	Enthalpy and Spontaneity		Determination of Absolute Entropy
	Entropy		Residual Entropy
	Entropy Changes in Some Simple Processes	4.6	Summary
	Entropy and Spontaneity	4.7	Terminal Questions
		4.8	Answers

## 4.1 INTRODUCTION

---

In the previous unit you have learnt about thermochemistry i.e., application of the First Law of thermodynamics to the study of heat changes associated with chemical reactions. In the last unit of this block we would take up Second and the Third Laws of thermodynamics. You would recall that the First Law of thermodynamics concerns about the conservation of energy. However, it does not say anything about the direction in which thermodynamic processes may proceed. The direction of thermodynamic processes is the subject matter of the Second Law of thermodynamics.

To learn about the Second Law we would begin by initiating a discussion on spontaneity and the need for a criterion for the same. For this we would take up spontaneous and non-spontaneous processes and check whether the internal energy and enthalpy, the two thermodynamic properties related to the first law, could serve as criterion for spontaneity? This will be followed by introduction of the concept of entropy-another state function. This would also be put to test as a criterion for spontaneity. Then we would take up different statements of the Second Law of thermodynamics.

Having learnt about the Second Law of thermodynamics we would briefly discuss about an important thermodynamic parameter viz., Gibbs energy and outline its significance and properties. Thereafter, we would move to the Third Law of thermodynamics. After stating the law we would introduce absolute entropy and take up its determination for a system. Towards the end of the unit we would explain the concept of residual entropy. In the next block you would learn about the chemical and ionic equilibrium.

## Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ explain spontaneous and non-spontaneous processes giving suitable examples;
- ❖ establish the inadequacy of enthalpy as a criteria for spontaneity using suitable examples;
- ❖ explain the concept of entropy as a measure of dispersal of energy and matter;
- ❖ give the thermodynamic and statistical definitions of entropy;
- ❖ explain the statistical viewpoint of entropy;
- ❖ demonstrate that entropy can act as a thermodynamic criteria for spontaneity of a reaction;
- ❖ give different statements of the Second Law of thermodynamics;
- ❖ define Gibbs energy and outline its significance;
- ❖ explain the difference between enthalpy driven and entropy driven reactions;
- ❖ ascertain using the data whether a given reaction is enthalpy driven or entropy driven;
- ❖ state and give significance of the Third Law of thermodynamics;
- ❖ determine the absolute entropy for a given system using the provided data;
- ❖ define and explain the concept of residual entropy for a system; and
- ❖ explain the meaning of the Third Law entropy for a system.

## 4.2 SPONTANEITY

One of the most significant considerations for a practicing Chemist when s/he is planning a new chemical reaction is that whether or not would the reaction occur under given set of conditions—say at room temperature and pressure? In other words, would the reaction be spontaneous? A criterion to determine the

spontaneity of a reaction is provided by the Second Law of thermodynamics in terms of the thermodynamic property called entropy (S). Let's first learn about the spontaneous and non-spontaneous processes to understand about entropy and its suitability as a criterion for spontaneity.

### 4.2.1 Spontaneous and Non-Spontaneous Processes

You must have seen and enjoyed a waterfall from a hill either in person or in a movie / picture. The water always flows downhill and never in the reverse direction on its own. Have you ever wondered why? It is an example of a **spontaneous process**—*a process that occurs on its own under a given set of conditions without the aid of any external agency*. That is once the process is started, no action from outside the system is necessary to make it to continue. We have a number of examples of spontaneous processes. Some of these being

- Hot water kept in a bucket cools down to the room temperature over a period of time,
- Water kept in a refrigerator maintained at  $-5^{\circ}\text{C}$  freezes spontaneously,
- Ice melts spontaneously at room temperature of say 298 K,
- A ball bouncing on the floor gradually comes to rest on the floor,
- An iron nail kept in open spontaneously gets rusted,
- A cube of sugar added to a glass of water dissolves spontaneously,
- A drop of ink added to a beaker of water spreads till the water is uniformly coloured,
- A puff of scent anywhere in the room spreads all over the room

You can visualise that, none of these processes occur in the reverse direction on their own. Water at room temperature (say 298 K) would not become hot or freeze on its own; the dissolved sugar would not come out of solution; the rusted nail would not get converted into clean nail on its own; a ball kept on the floor will not start bouncing by itself. Such processes are called

**non-spontaneous processes**. We need to supply energy in some form or the other for such non-spontaneous processes to occur. A book kept at the edge of a table may fall down spontaneously but someone would have to pick up and keep it back; it won't happen on its own. You may note here that *if a physical or a chemical change is spontaneous in one direction, it is not spontaneous in the opposite direction*. Secondly, *both spontaneous and non-spontaneous processes are possible, but only spontaneous processes occur on their own; the non-spontaneous processes require the help of an external agent to occur*.

You should keep in mind that thermodynamic spontaneity is not related to the speed of the reaction or the process. A reaction being spontaneous does not mean that it would occur very fast or at a measurable rate. For example, the reaction between hydrogen and oxygen gas to give water is a spontaneous reaction but under ordinary conditions we can keep hydrogen and oxygen together for any length of time without getting even a trace of water. The rate

Spontaneous does not mean instantaneous and has nothing to do with how long a process takes to occur. It means that if enough time is given, the process will happen by itself. There are many processes that are spontaneous but very slow for example, rusting of iron, ripening of fruits and aging.

of the reaction comes in the domain of Chemical Kinetics about which you would learn in a later course. For now, let's raise a question, "Can the First Law of thermodynamics explain spontaneity of physical and chemical processes"?

To answer this question we take the example of the water in a river flowing down a hill. As the water flows down it loses its potential energy, which is converted into the kinetic energy of the molecules. If we account for the frictional losses during its flow we can find that the loss in potential energy of water is exactly equal to the gain in its kinetic energy. This is as expected from the First Law of thermodynamics according to which the total energy remains constant. On the other hand, though we have never seen rivers flowing upwards, if the river could flow upwards the kinetic energy of the flowing water would be converted into its potential energy such that the total energy remains constant. That is, in principle such a process is not ruled out according to the First Law. In other words, we can say that according to the First Law of thermodynamics the water in river may flow downhill or uphill. However, our experience tells us that the river flows *only* downhill on its own. This is a serious limitation of the First Law that it does not say anything about the directionality or spontaneity of a process.

Let's see whether energy (enthalpy) change for a process can act as criterion for spontaneity?

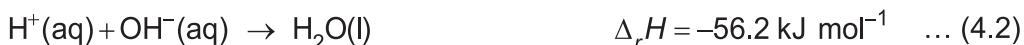
### **4.2.2 Enthalpy and Spontaneity**

Let's revisit the examples of waterfall and the book falling from the table. We note here that in both of these cases the potential energy of the system decreases. Internal energy or the related thermodynamic property, enthalpy is analogous to the energy of a mechanical system. Then, can we say that 'decrease in internal energy or enthalpy' makes a process spontaneous? In fact P. Berthelot and J. Thomsen proposed in 1870s that the spontaneous processes occur in the direction in which the enthalpy of the system decreases. This proposal got support from the fact that a number of spontaneous chemical reactions were found to be exothermic, i.e., accompanied by a decrease in enthalpy. Some of the common examples of spontaneous exothermic reactions are

#### **Combustion of methane**



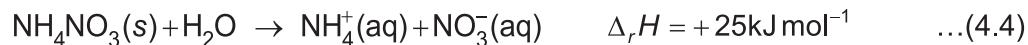
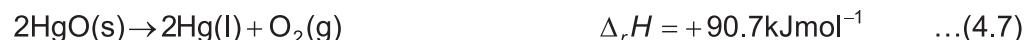
#### **Acid-base neutralization**



#### **Rusting of iron**



On the other hand, there are a number of spontaneous chemical reactions and physical processes that are endothermic, i.e., accompanied by an increase in enthalpy. Some examples being,

**Dissolution of ammonium nitrate****Decomposition of nitrogen pentaoxide****Evaporation of water at room temperature****Decomposition mercury(II) oxide at high temperature**

From these examples we can infer that the exothermic nature of a reaction or process favours its spontaneity however it does not guarantee the same. In other words, we **cannot** use enthalpy (or internal energy) as a criterion for spontaneity.

The natural direction of spontaneous processes in the examples stated above can be easily judged by observing the initial and final states of the system. This in turn suggests that we may have a new *state function* that could predict the directionality of spontaneous processes. That is, in order to predict the spontaneity of a chemical reaction we need a yet another thermodynamic property that happens to be a state function. This property is entropy about you would learn in the next subsection. However, before that answer the following simple self assessment question.

**SAQ 1**

What are spontaneous reactions? Can internal energy serve as a criterion for spontaneity of a chemical reaction?

**4.2.3 Entropy**

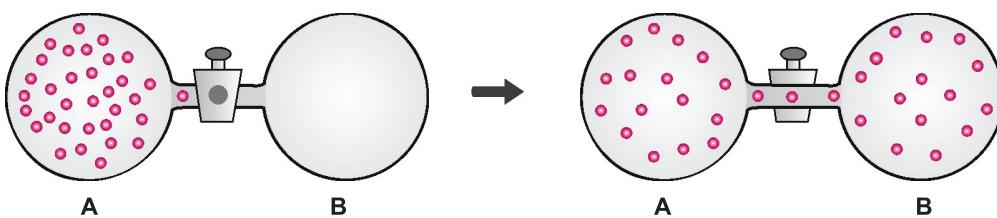
In order to explain the direction of spontaneous change, German physicist and mathematician Rudolf Clausius introduced the concept of entropy—a new thermodynamic quantity in 1865. More than two decades later Austrian physicist and philosopher, Ludwig Boltzmann proposed a statistical view of entropy. The two views were later shown to be equivalent. In order to understand about entropy let's take some of the examples of spontaneous processes given above and analyse them.

- The first example we take is, “hot water kept in a bucket cools down to the room temperature over a period of time”. In this case to begin with the molecules of hot water and the molecules constituting the bucket have high kinetic energy (you know that the kinetic energy is proportional to the absolute temperature). This energy is dissipated (or is dispersed) to the molecules of air in the immediate vicinity and the floor where the bucket is kept. Over a period of time, due to the random motion of the molecules of

the air and the floor this energy is further spread out to infinite surroundings. The process is spontaneous and continues till the temperatures of the water in bucket and the surroundings become equal. The reverse of all this is improbable. It can never happen that the molecules of air surrounding the bucket or the floor, at the same temperature as the bucket and the water in it, transfer their energy to the water in the bucket and it becomes hot. From this we can conclude that the energy of a system spontaneously “spreads out” or “disperses”.

- As the second example let's consider another spontaneous process, viz., “puff of scent anywhere in the room spreads all over the room”. When we open a bottle of scent anywhere in the room the molecules of scent spontaneously spread out to the whole room. The reverse never happens i.e., the perfume spread in a room does not on its own accumulate and get back into the bottle (it is like running a film in the reverse direction). Here what we observe is that like energy, matter also spontaneously “spreads out or disperses”.
- We can also consider the example of spontaneous evaporation of water though it is an endothermic process. This phase change involves going from a state (liquid) with water molecules having limited freedom to move around each other, to a state (gas) with much greater freedom of particle motion.
- Similarly, in the case of another endothermic process viz., dissolution of ammonium nitrate involves a change from initial state of an ordered crystalline solid and relatively less ordered pure liquid to final state of highly disordered ions and solvent molecules moving and interacting throughout the solution. Here again, the energy of motion of particles is much more dispersed in the spontaneous process.

In addition to the examples discussed above, let's perform an experiment to understand entropy. Let's consider two glass flasks having equal volumes ( $V$ ) interconnected by a stopcock as shown in the Fig. 4.1. One of these flasks (say A) contains a certain amount of an ideal gas at a certain pressure (say 1 bar) while the other flask (B) is fully evacuated. The whole apparatus is immersed in a thermostat so that the temperature remains constant throughout the process. Now, when we open the stopcock, the gas in flask A spontaneously expands into the evacuated flask B. The molecules get dispersed throughout the apparatus, such that both the flasks have equal numbers of gas molecules. As after expansion the ideal gas occupies double its initial volume the pressure becomes half i.e., 0.5 bar.



**Fig. 4.1: Demonstrating that spontaneous expansion of a gas against vacuum leads to dispersal of energy.**

In this spontaneous process, the change in internal energy ( $\Delta U$ ) would be zero as the temperature of the system does not change and for an ideal gas the internal energy depends on the temperature.

Further, as the gas expands into vacuum i.e., against zero opposing pressure, the work of expansion ( $pdV$ ) is also zero. Therefore, as a result, the enthalpy change ( $\Delta H = \Delta U + pdV$ ) for the process is zero. Now, neither the internal energy is changed nor the enthalpy, then what causes this process to happen on its own? Since the volume available to the gas has increased there is much greater freedom of particle motion. In other words, the energy of motion is much more dispersed. It is this dispersal of energy that is the 'driving force' behind the spontaneous process.

The dispersal of matter leads to more disorder. Therefore, entropy can be taken as a measure of disorder. As we heat a solid to its melting point the particles in the liquid so obtained are more disordered. Similarly when we heat a liquid to convert it to a gas then there is much more disorder. Hence, the entropy varies as  $g > l > s$

On the basis of the examples considered above, we can conclude that a change in the freedom of motion of particles in a system and the dispersal of their energy of motion is important in determining the direction of a spontaneous process. The dispersal of energy is measured in terms of a thermodynamic property called **entropy**; greater the dispersal, greater is the entropy. Like internal energy and enthalpy, entropy is also a state function; that is it depends on the initial and final states of the system and does not depend on how (the path taken) the final state has been achieved. Having got some kinds of a mental picture of entropy now let's give a thermodynamic definition to it.

### Thermodynamic Definition of Entropy

The thermodynamic property identified with this dispersal of energy in spontaneous processes as discussed above is called entropy. It is denoted as  $S$  and defined as per the following equation

$$dS = \frac{dq_{rev}}{T} \quad \dots (4.8)$$

Where,  $dq_{rev}$  is the infinitesimal heat exchange between the system and the surroundings at temperature,  $T$  K. The importance of Eq. (4.8) is that it relates a small change in entropy,  $dS$  to quantities that are easily interpreted i.e., heat and temperature of the system. Further, since entropy is defined as a ratio of  $q$  to  $T$  ( $q/T$ ) its units are  $J\ K^{-1}$ . However, to calculate the entropy change for a system using this expression, we must devise a way to accomplish a given change in a reversible way i.e., the one occurring in an infinite number of infinitesimal steps. So the finite change in entropy  $S_f - S_i$  of the system during a process that takes the system from an initial state  $i$  into a final state  $f$  can be obtained by integrating Eq. (4.8) i.e.,

$$\Delta S = S_f - S_i = \int_i^f \frac{dq_{rev}}{T} \quad \dots (4.9)$$

You must remember that the entropy change in a system is calculated by assuming the process to be reversible, irrespective of the fact that whether the process is reversible or not. We would calculate the entropy changes associated with different processes. However, before that let us learn about the statistical definition of entropy.

### Statistical definition of entropy

We have so far talked qualitatively about entropy as a measure of more disorderly distribution of matter and a greater dispersal of energy. Austrian mathematician and physicist **Ludwig Boltzmann** in 1877 provided a quantitative interpretation of these in terms of number of microstates i.e., *the number of ways in which the molecules of a system can be arranged while keeping the total energy of the system constant*. He proposed that the entropy of a system is given by the following expression.

$$S = k \ln W \quad \dots (4.10)$$

Where,  $k$  is the Boltzmann constant ( $=1.381 \times 10^{-23} \text{ J K}^{-1}$ ) and  $W$  is the number of microstates. It is obvious that a state with more microstates has greater entropy. In order to understand the concept let us consider a hypothetical system with four molecules in a container, which is divided (by an imaginary partition) into two equal parts as shown in Fig. 4.2. Let us label these parts as part A and part B. Now we try to think of different possibilities of the distribution of the molecules in the box. In one of the ways, all the molecules can be in the part A and none in part B. There is only one way to arrange the molecules like this. Now suppose we distribute the molecules in such a way that the part A has three molecules and part B has only one molecule. There are four different possible arrangements as shown in the figure.

Boltzmann constant can be seen as universal gas constant divided by Avogadro's number, i.e., gas constant per molecule;  $R / N_A$

If we continue and distribute the molecules equally in the two parts such that each part has two molecules then there are six different possible arrangements as shown. Similarly we can show that there are four different ways of arranging one molecule in the part A and three molecules in part B. Once again there is only one way of arranging molecules such that all the four molecules are in part B and none in part A. Thus, there are a total of sixteen different ways of arranging 4 molecules in two parts of the box.

For  $N$  molecules there are  $2^N$  different possibilities

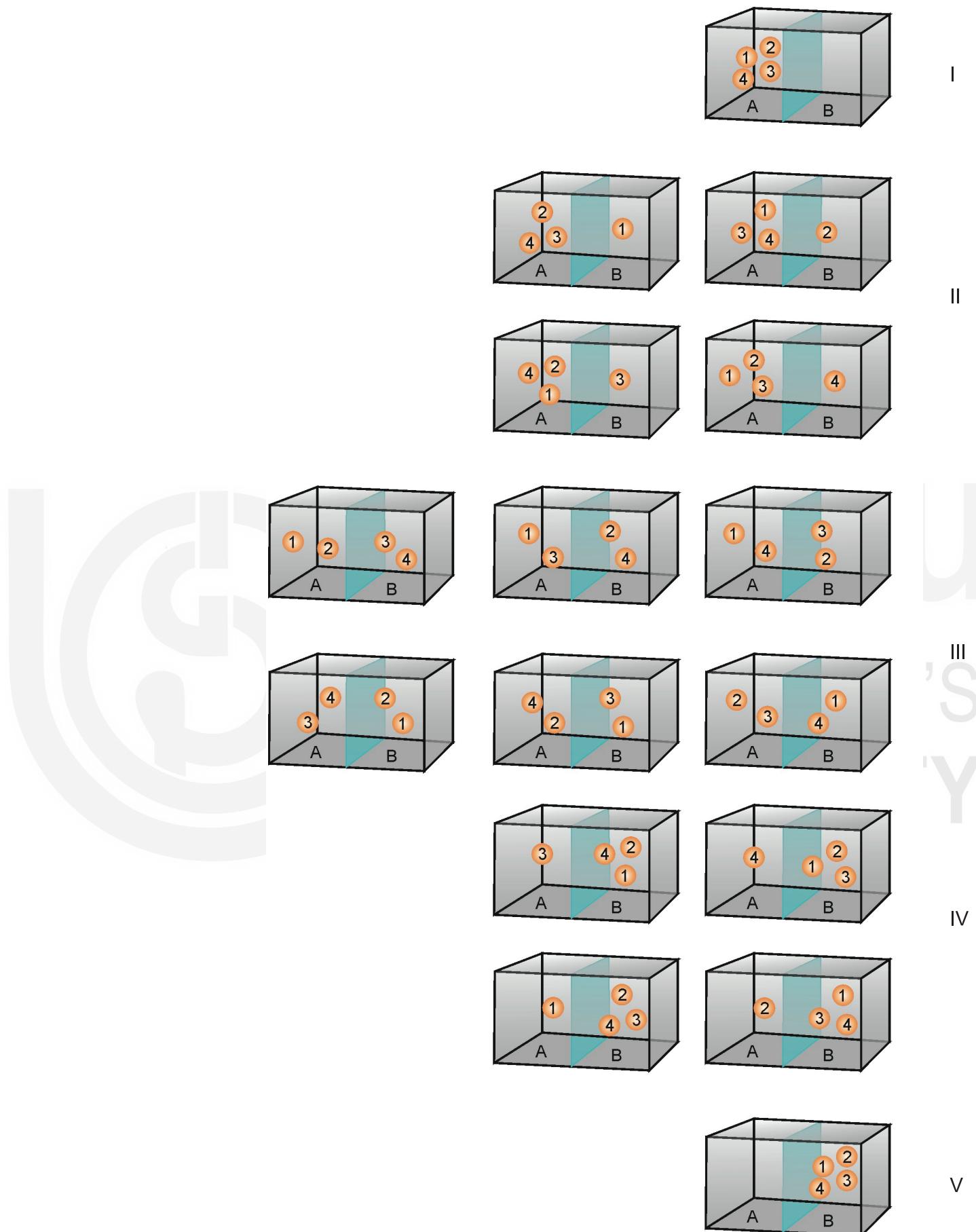
The sixteen possible different ways of distributing the molecules shown in the figure are called microscopic states or *microstates*. Further, each set of similar microstates is called a *distribution* or a *state*. The probability of a particular distribution depends on the number of microstates in it. In this example, we have five different states or distributions (I-V). You can note that of the possible distributions, the distribution III is the most probable as this can be achieved in six possible ways or has six microstates. On the other hand, the distributions I and V are least probable with only one microstate each. Thus, we can see that the state with even (equal) distribution of molecules in the two parts is most probable.

The entropy change for a process in which the system goes from an initial state  $i$  to final state  $f$  can be given as

$$\Delta S = S_f - S_i = k \ln W_f - k \ln W_i \quad \dots (4.11)$$

$$\Delta S = k \ln \frac{W_f}{W_i} \quad \dots (4.12)$$

Where  $S_i$  and  $S_f$  are the entropies of the system in the initial and final states and  $W_i$  and  $W_f$  are the corresponding numbers of microstates.



**Fig. 4.2: Different possible ways of distributing four molecules in two equal parts of a box.**

If the number of microstates in the final state ( $W_f$ ) is greater than that in the initial state ( $W_i$ ) then  $\Delta S$  is positive i.e., entropy increases. On the other hand, if the number of microstates in the final state is lesser the entropy decreases. On the basis of what you have learnt about entropy answer the following simple question.

## **SAQ 2**

State whether the entropy of the system would increase or decrease in the following processes.

- i) Condensation of a gas to form a liquid
- ii) Crystallisation from a saturated solution
- iii) Sublimation of a solid
- iv) Dissolution of sucrose in water

### **4.2.4 Entropy Changes in Some Simple Processes**

Having learnt about the thermodynamic and statistical definitions of entropy let's calculate the entropy changes associated with some simple processes. We start with the isothermal expansion of an ideal gas.

#### **a) Reversible Isothermal Expansion of an Ideal Gas**

Let's take 1 mole of an ideal gas having a volume of  $V_1$  at a pressure  $p_1$  and expand it reversibly to a volume  $V_2$  under isothermal conditions i.e., the temperature is maintained at  $T$  K. For such a process the Eq. (4.9) becomes

$$\Delta S = \frac{1}{T} \int_i^f dq_{rev} = \frac{q_{rev}}{T} \quad \dots(4.13)$$

Further, you would recall again that in such an isothermal process the change in internal energy would be zero ( $\Delta U=0$ ) as for an ideal gas the internal energy depends on temperature of the system and here the temperature does not change. Also, from the First Law of thermodynamics, we can write

$$\Delta U = q + w \quad \dots(2.1)$$

In the present context (reversible expansion) we can write,

$$\Delta U = q_{rev} + w_{rev} \quad \dots(4.14)$$

Now, since  $\Delta U=0$  we can write

$$0 = q_{rev} + w_{rev} \Rightarrow q_{rev} = -w_{rev} \quad \dots(4.15)$$

From Unit 2 you would recall that the expression for work for isothermal reversible expansion of an ideal gas is given by Eq. (2.66),

$$w_{rev} = -2.303 nRT \log \frac{V_2}{V_1} \quad \dots(2.66)$$

Substituting in Eq. (4.15) we get,

$$q_{rev} = -w_{rev} = -(-2.303 nRT \log \frac{V_2}{V_1}) = 2.303 nRT \log \frac{V_2}{V_1} \quad \dots(4.16)$$

Substituting Eq. (4.16) in Eq. (4.13) we get

$$\Delta S = \frac{q_{rev}}{T} = \frac{1}{T} (2.303 nRT \log \frac{V_2}{V_1})$$

$$\Rightarrow \Delta S = 2.303 nR \log \frac{V_2}{V_1} \quad \dots(4.17)$$

We know that for an ideal gas  $p_1V_1 = p_2V_2$ , so we can replace  $\frac{V_2}{V_1}$  in Eq. (4.17)

by  $\frac{p_1}{p_2}$  to get,

$$\Rightarrow \Delta S = 2.303 nR \log \frac{p_1}{p_2} \quad \dots(4.18)$$

Thus, Eq. (4.17) and Eq. (4.18) are the desired expressions to compute entropy change for reversible isothermal expansion of an ideal gas. The corresponding expressions for one mole of an ideal gas (or molar entropy changes) would be:

$$\Rightarrow \Delta S_m = 2.303 R \log \frac{V_2}{V_1} \quad \dots(4.19)$$

$$\Rightarrow \Delta S_m = 2.303 R \log \frac{p_1}{p_2} \quad \dots(4.20)$$

As per Eq. (4.17) for reversible isothermal expansion of an ideal gas the entropy change would be positive, i.e., the entropy would increase. From the same expression we can conclude that in case of isothermal compression since  $V_2$  will be less than  $V_1$  the entropy would decrease. Let us take an example to see the application of the expression derived above.

**Example 4.1:** 1 mole of neon gas behaving ideally is taken in a cylinder fitted with massless and frictionless piston and occupies a volume of  $10 \text{ dm}^3$ . If the gas is reversibly expanded to double its volume at 298 K, calculate the entropy change for the process.

**Solution:** The entropy change for reversible isothermal expansion of a gas is given by the following expression; Eq. (4.17).

$$\Rightarrow \Delta S = 2.303 nR \log \frac{V_2}{V_1}$$

The data provided is as under

$$n = 1.00 \text{ mol} \quad V_1 = 10 \text{ dm}^3 \quad V_2 = 20 \text{ dm}^3$$

$$R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}$$

Substituting the values in the equation we get

$$\Rightarrow \Delta S = 2.303 \times 1.0 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \log \frac{20}{10}$$

$$\Rightarrow \Delta S = 19.147 \text{ J K}^{-1} \log 2 = 5.76 \text{ J K}^{-1}$$

### b) Adiabatic Expansion of an Ideal Gas

As you know that in an adiabatic process, there is no associated heat change i.e.,  $q = 0$  therefore, the entropy change would be

$$\Delta S = \frac{q_{rev}}{T} = 0$$

### c) Isothermal Mixing of Ideal Gases

Let us take  $n_A$  moles of an ideal gases A and  $n_B$  moles of ideal gas B at same pressure in two glass flasks (A and B) of respective volumes of  $V_A$  and  $V_B$  connected by a stopcock as shown in Fig. 4.3 (a). The whole system is placed in a thermostat to keep the temperature constant. On opening the stopcock the two gases mix spontaneously Fig. 4.3 (b). The process can be represented as

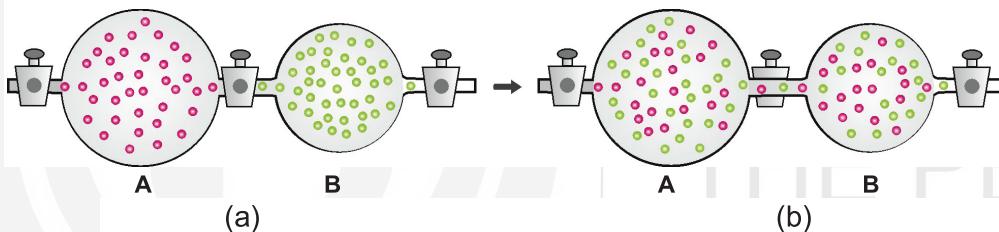
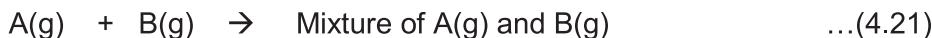


Fig. 4.3: Isothermal mixing of ideal gases.

After mixing both the gases occupy a final total volume ( $= V_A + V_B$ ). Therefore, the mixing process can be assumed to be equal to combined effect of A(g) and B(g) expanding to a final volume of  $V_A + V_B$  from their respective initial volumes of  $V_A$  and  $V_B$  respectively. We can write the corresponding isothermal entropy changes by using Eq. (4.17), as below

$$\text{For expansion of } A(g) \Rightarrow \Delta S_{A(g)} = 2.303 n_A R \log \frac{V_A + V_B}{V_A} \quad \dots(4.22)$$

$$\text{For expansion of } B(g) \Rightarrow \Delta S_{B(g)} = 2.303 n_B R \log \frac{V_A + V_B}{V_B} \quad \dots(4.23)$$

The total entropy change for the mixing process is equal to the sum of the entropy changes of expansion of A(g) and B(g):

$$\Delta S_{\text{mixing}} = \Delta S_{A(g)} + \Delta S_{B(g)} \quad \dots(4.24)$$

$$\Delta S_{\text{mixing}} = 2.303 R \left[ n_A \log \frac{V_A + V_B}{V_A} + n_B \log \frac{V_A + V_B}{V_B} \right] \quad \dots(4.25)$$

In the mixture of gases the mole fractions of the gases would be

We know that for an ideal gas

$$pV = nRT$$

$$\Rightarrow V = nRT / p$$

If  $p, R$  and  $T$  are const.

$n \propto V$

$$n_A \propto V_A; n_B \propto V_B$$

$$n_T \propto V_A + V_B$$

$$X_A = \frac{n_A}{n_A + n_B} = \frac{V_A}{V_A + V_B}$$

$$X_B = \frac{n_B}{n_A + n_B} = \frac{V_B}{V_A + V_B}$$

$$\text{Mole fraction of A(g)} = X_A = \frac{V_A}{V_A + V_B} \quad \dots(4.26)$$

$$\text{Mole fraction of B(g)} = X_B = \frac{V_B}{V_A + V_B} \quad \dots(4.27)$$

Substituting Eq. (4.26) and Eq. (4.27) in Eq. (4.25), we get

$$\Delta S_{mixing} = 2.303R \left[ n_A \log\left(\frac{1}{X_A}\right) + n_B \log\left(\frac{1}{X_B}\right) \right] \quad \dots(4.28)$$

$$\Delta S_{mixing} = 2.303 R [ -n_A \log(X_A) - n_B \log(X_B)] \quad \dots(4.29)$$

$$\Delta S_{mixing} = -2.303 R [ n_A \log(X_A) + n_B \log(X_B)] \quad \dots(4.30)$$

As the values of mole fractions of the two gases are less than 1; their logs will be negative so both the terms in the bracket would be negative. This implies that  $\Delta S_{mixing}$  of the gases would be positive.

#### d) Expansion and Heating of an Ideal Gas

In the cases considered above we have taken systems where only one parameter viz., the volume is allowed to change during the process. We may have thermodynamic processes wherein more than one of the thermodynamic parameters of the system can change. Such processes are called composite processes. Let us consider one such process wherein a gaseous system at initial state characterised by  $(V_1, T_1)$  changes to final state  $(V_2, T_2)$ . That is in this case both the volume and the temperature of the gas is different in the initial and final states.

In order to compute the associated entropy change, we make use of the fact that the entropy is a state function. Since entropy is a state function, we can choose any convenient path to go from the initial state to the final state. We can achieve the given changes in the thermodynamic parameters of the system by first considering reversible isothermal expansion of the gas from volume  $V_1$  to volume  $V_2$  at temperature  $T_1$ , followed by reversible heating of the gas at constant volume ( $V_2$ ) to the final temperature  $T_2$ . The total entropy change would be the sum of the two contributions.

$$(V_1, T_1) \xrightarrow{\text{I}} (V_2, T_1) \xrightarrow{\text{II}} (V_2, T_2) \quad \dots(4.31)$$

For the first step we can write the entropy change by using Eq. (4.17)

$$\Rightarrow \Delta S_I = 2.303 nR \log \frac{V_2}{V_1}$$

For second step, as the process involves reversibly heating the gas at constant volume (i.e.,  $\Delta V=0$ ) which means that  $w=0$ . In such a case we can write from the First Law expression (Eq. 2.1)

$$\Delta U = q_{rev}$$

From Eq. (2.21) we know that

$$\Delta U = C_V dT$$

Therefore, we can write

$$\Delta S_{II} = \frac{q_{rev}}{T} = \int_{T_1}^{T_2} \frac{C_V dT}{T} \quad \dots(4.32)$$

Taking  $C_V$  out of the integration sign and integrating the equation, we get

$$\Delta S_{II} = C_V \int_{T_1}^{T_2} \frac{dT}{T} = C_V \left[ \ln T \right]_{T_1}^{T_2} \quad \dots(4.33)$$

$$\Delta S_{II} = C_V \ln \frac{T_2}{T_1} = 2.303 \log \frac{T_2}{T_1} \quad \dots(4.34)$$

Thus, the overall entropy change for the process would be

$$\Rightarrow \Delta S_I + \Delta S_{II} = 2.303 \left[ nR \log \frac{V_2}{V_1} + C_V \log \frac{T_2}{T_1} \right] \quad \dots(4.35)$$

Let us take an example to see the application of this expression:

**Example 4.2:** One mole of an ideal gas is taken in a cylinder fitted with massless and frictionless piston and occupies volume of  $2 \text{ dm}^3$  at  $298 \text{ K}$ . The gas is isothermally and reversibly expanded to ten times its initial volume at  $298 \text{ K}$ . After this the gas is reversibly heated at constant volume to  $323 \text{ K}$ . Calculate the entropy change for the overall process. The heat capacity of the gas at constant volume in the range of temperature is given as  $12.47 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**Solution:** As stated there are two stages in the process i.e., isothermal reversible expansion of the ideal gas and isochoric reversible heating of the gas. Let's compute the entropy changes for the two stages one by one.

Stage 1: From Eq. (4.17) the entropy change for isothermal reversible expansion of the ideal gas is given as

$$\Rightarrow \Delta S_I = 2.303 nR \log \frac{V_2}{V_1}$$

We are given  $n = 1 \text{ mol}$ ;  $V_1 = 2 \text{ dm}^3$ ;  $V_2 = 20 \text{ dm}^3$

We know  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Substituting the values in the equation, we get

$$\Rightarrow \Delta S_I = 2.303 \times 1.0 \text{ mol} \times (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \log \frac{20}{2}$$

Solving, we get,

$$\Rightarrow \Delta S_I = 19.15 \text{ J K}^{-1}$$

Stage 2: For isochoric reversible heating of an ideal gas the molar entropy change can be calculated by using Eq. (4.34)

$$\Delta S_{II} = C_V \ln \frac{T_2}{T_1} = 2.303 C_V \log \frac{T_2}{T_1}$$

We are given  $C_{V,m} = 12.47 \text{ J K}^{-1}\text{mol}^{-1}$   $T_1 = 298 \text{ K}$   $T_2 = 323 \text{ K}$

Substituting the values in the expression, we get

$$\Delta S_{II} = 2.303(12.47 \text{ J K}^{-1} \text{ mol}^{-1}) \log \frac{323}{298}$$

Solving, we get

$$\Delta S_{II} = 1.005 \text{ J K}^{-1}\text{mol}^{-1}$$

Total entropy change for the overall process would be

$$\Rightarrow \Delta S_I + \Delta S_{II} = 19.15 \text{ J K}^{-1}\text{mol}^{-1} + 1.005 \text{ J K}^{-1}\text{mol}^{-1} = 20.155 \text{ J K}^{-1}\text{mol}^{-1}$$

### e) Phase Transformation

We know that matter exists in different physical states (solid, liquid, gas, crystalline forms) called phases. The matter in a given phase can change into another phase under appropriate conditions, for example, a solid transforms into a liquid at its melting point. The change of matter from one phase into another phase is called *phase transition* and the temperature at which these occur are called *transition temperatures* at a given pressure. The change of entropy accompanying the transformation of one mole of a substance from one physical state into another physical state at its transition temperature is called *entropy of phase transformation*. It is denoted as  $\Delta_{tr}S$  and is defined as

$$\Delta_{tr}S = \frac{q_{tr}}{T_{tr}} = \frac{q_{rev}}{T_{tr}} \quad \dots(4.36)$$

The Eq. (4.36) is valid only when the two phases are in equilibrium. Further, as we know that for a process at constant pressure  $q_p = \Delta H$ , therefore, we can write,

$$\Delta_{tr}S = \frac{\Delta_{tr}H}{T_{tr}} \quad \dots(4.37)$$

Different phase transitions are identified in terms of the process involved. For example, when one mole of a liquid vaporises to gaseous phase the entropy change is given as under

$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T_b} \quad \dots(4.38)$$

Where,  $\Delta_{\text{vap}}H$  is the enthalpy of vaporization of the liquid;  $T_b$  is the boiling point of the liquid and  $\Delta_{\text{vap}}S$  is the entropy of vaporisation. Similarly, when one mole of a solid melts to give liquid the entropy change is given by the following expression

$$\Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T_f} \quad \dots(4.39)$$

$\Delta_{\text{fus}}H$  is the enthalpy of fusion of the liquid;  $T_f$  is the melting point of the liquid and  $\Delta_{\text{fus}}S$  is the entropy of fusion. It is important to note that the entropy of the reverse processes would be negative of the given process. For example, the entropy of condensation of vapors to liquid phase would be  $-\Delta_{\text{vap}}S$ . Let us take an example for the calculation of entropy change associated with phase transition.

**Example 4.3:** Elemental sulphur undergoes a phase transition from orthorhombic form to monoclinic form at 363 K. If the molar enthalpy of transition is  $-402 \text{ J mol}^{-1}$ , calculate the entropy of transition.

**Solution:** The entropy change for phase transition is given by Eq. (4.37)

$$\Delta_{\text{tr}}S = \frac{\Delta_{\text{tr}}H}{T_{\text{tr}}}$$

We are provided with the enthalpy change and the temperature for the transition of elemental sulphur from orthorhombic to monoclinic form. The calculation of the entropy change is quite straightforward.

Substituting the values in the expression, we get

$$\Delta_{\text{tr}}S = \frac{-402 \text{ J mol}^{-1}}{363 \text{ K}} = -1.107 \text{ J K}^{-1}\text{mol}^{-1}$$

Having learnt about entropy and entropy changes in different types of processes, let's now check whether it can serve as a criterion for spontaneity?. However, before that answer the following simple questions

### SAQ 3

One mole each of two ideal gases at same pressure are taken in two separate containers interconnected with a valve and having volumes of  $5 \text{ dm}^3$  and  $10 \text{ dm}^3$  respectively at  $298 \text{ K}$ . On opening the interconnecting valve the gases are allowed to mix. Calculate the entropy of mixing of the gases at  $298 \text{ K}$ .

### SAQ 4

At a pressure of 1 bar, water undergoes fusion at  $273.1 \text{ K}$ . Write the equation for the process. Calculate the entropy of fusion of water if the molar enthalpy of fusion of water is found to be  $6.02 \text{ kJ mol}^{-1}$ .

## 4.2.5 Entropy and Spontaneity

We had demonstrated above that the internal energy and enthalpy do not serve as a criterion to determine the spontaneity of a thermodynamic process. Now, having learnt about a new state function viz., entropy let us evaluate it as a criterion for spontaneity. For this we take up entropy changes in isolated systems. We begin with an isolated system involving a cyclic process of isothermal expansion and compression.

### a) Cyclic Isothermal Reversible Expansion and Isothermal Reversible Compression in an Isolated System

Let's take a certain amount of an ideal gas occupying a volume  $V_1$  in a cylinder fitted with a massless and frictionless piston. The system is maintained at temperature  $T$  in a thermostat. Now if the gas expands reversibly from the initial volume  $V_1$  to  $V_2$ , the system would absorb heat equal to  $q_{rev}$  from the surroundings and the associated entropy change of the system would be

$$\Delta S_{sys} = \frac{q_{rev}}{T} \quad \dots(4.8)$$

Since the surroundings also loses heat equal to  $-q_{rev}$  in a reversible way, the entropy change, for the surroundings would be

$$\Delta S_{surr} = -\frac{q_{rev}}{T} \quad \dots(4.40)$$

The total entropy change for the isothermal reversible expansion process in the isolated system would be

$$\Delta S_{isoth\ exp} = \Delta S_{sys} + \Delta S_{surr} = \frac{q_{rev}}{T} + \left(-\frac{q_{rev}}{T}\right) = 0 \quad \dots(4.41)$$

Once the gas has been reversibly expanded to a volume  $V_2$  under isothermal conditions, we reversibly compress it back to volume  $V_1$  again under isothermal conditions. In such a case the system would lose heat equal to  $-q_{rev}$  to the surroundings and the corresponding entropy change for the system would be

$$\Delta S_{sys} = -\frac{q_{rev}}{T} \quad \dots(4.42)$$

As the surrounding would gain heat equal to  $q_{rev}$ , the associated entropy change would be

$$\Delta S_{surr} = \frac{q_{rev}}{T} \quad \dots(4.43)$$

The total entropy change in the isolated system for the isothermal reversible compression process would be

$$\Delta S_{isoth\ comp} = \Delta S_{sys} + \Delta S_{surr} = -\frac{q_{rev}}{T} + \frac{q_{rev}}{T} = 0 \quad \dots(4.44)$$

The entropy change for the overall reversible cyclic process in the isolated system would be

$$\Delta S_{\text{cyclic}} = \Delta S_{\text{isoth exp}} + \Delta S_{\text{isoth comp}} = 0 + 0 = 0 \quad \dots(4.45)$$

Thus, we see that overall entropy change in a reversible cyclic process in an isolated system is zero. Let us now calculate the entropy changes in a cyclic process having an irreversible step.

### b) Cyclic Isothermal Irreversible Expansion and Isothermal Reversible Compression in an Isolated System

Let's again take a certain amount of an ideal gas occupying a volume  $V_1$  in a cylinder fitted with a massless and frictionless piston. The system is maintained at temperature  $T$  in a thermostat. Let us assume that the gas expands against zero opposing pressure (free expansion; irreversible process) from the initial volume  $V_1$  to  $V_2$ . In this case, as we have discussed before the change in internal energy,  $\Delta U=0$  and also work,  $pdV=0$  [the opposing pressure is zero] so according to the First Law of thermodynamics

$$\Delta U = q + w \Rightarrow 0 = q + 0 \Rightarrow q = 0 \quad \dots(4.46)$$

The heat absorbed by the system from the surrounding,  $q=0$ . However as per the definition the entropy change for the system would be

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T} \quad \dots(4.48)$$

Now, since the surroundings lost no heat the entropy change, for the surroundings would be

$$\Delta S_{\text{surr}} = 0 \quad \dots(4.47)$$

The total entropy change in the isolated system for the irreversible expansion process would be

$$\Delta S_{\text{isoth irr exp}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T} + 0 = \frac{q_{\text{rev}}}{T} \quad \dots(4.48)$$

Once the gas has been irreversibly expanded to a volume  $V_2$  under isothermal conditions, we reversibly compress it back to volume  $V_1$  under similar conditions. In such a case the system would lose heat equal to  $-q_{\text{rev}}$  to the surroundings and the corresponding entropy change would be

$$\Delta S_{\text{sys}} = -\frac{q_{\text{rev}}}{T} \quad \dots(4.49)$$

As the surrounding would gain heat equal to  $q_{\text{rev}}$  the associated entropy change would be

$$\Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T} \quad \dots(4.50)$$

The total entropy change in the isolated system for the isothermal reversible compression process would be

The energy of a closed system is conserved; it always remains constant. For irreversible processes, the entropy of a closed system always increases. Therefore, the change in entropy is sometimes called "the arrow of time."

All real processes occur spontaneously in the direction that increases the entropy of the universe (system plus surroundings)

According to the second law if a system is at equilibrium, then any infinitesimally small perturbation of the system will not change its total entropy i.e.,  $\Delta S=0$ . However, if the system is not at equilibrium, then a spontaneous change in the system will occur in such a way that the total entropy of the system and surroundings increases.

Freezing is an exothermic process; the heat transferred from the system to the surroundings increases disorder in the surroundings thereby increasing the entropy of surroundings.

$$\Delta S_{\text{isoth rev comp}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -\frac{q_{\text{rev}}}{T} + \frac{q_{\text{rev}}}{T} = 0 \quad \dots(4.51)$$

The overall entropy change for the cyclic process would be

$$\Delta S_{\text{cyclic}} = \Delta S_{\text{isoth irr exp}} + \Delta S_{\text{isoth rev comp}} = \frac{q_{\text{rev}}}{T} + 0 = \frac{q_{\text{rev}}}{T} > 0 \quad \dots(4.52)$$

Thus, we see that overall entropy change in a cyclic process involving an irreversible step in an isolated system is positive.

On the basis of the two cases of cyclic processes in isolated systems discussed here we can say that the entropy of the system plus the surroundings increases in case of a spontaneous (irreversible) process. In other words, we can say that for an isolated system the total entropy of the universe *increases in an irreversible process* and remains *constant for reversible processes*. However, it never decreases. Mathematically,

$$\Delta S_{\text{system}} + \Delta S_{\text{surr}} = \Delta S_{\text{total}} \geq 0 \quad \dots(4.53)$$

Thus, we see that entropy does provide a criterion for establishing the spontaneity of a process. This, in fact paves way for stating the Second Law of thermodynamics.

### 4.3 THE SECOND LAW OF THERMODYNAMICS

You would recall that in the beginning of the unit we discussed and showed that the First Law of thermodynamics concerns the conservation of energy, however, it does not tell anything about the 'directionality' of the process. In other words, according to the First Law of thermodynamics a system can in principle undergo any process as long as the energy is conserved. However, as we have just shown above that the natural (spontaneous) direction of a process i.e., of the possible processes, the one, which happens on its own, or the directionality of a process can be ascertained in terms of entropy. This leads us to state the Second Law of thermodynamics as

**Sum of the entropy of a system and its surroundings increases for a spontaneous process,  $\Delta S_{\text{total}} > 0$ .**

Further, we have shown that for non-spontaneous processes,  $\Delta S_{\text{total}} = 0$ . Thus, according to the Second Law of thermodynamics, a spontaneous process will be accompanied by an increase in  $\Delta S_{\text{total}}$  or  $(\Delta S_{\text{sys}} + \Delta S_{\text{surr}})$ . However, you

may note here that the Second Law places no limitations on the individual entropy changes of the system or the surroundings. The only requirement from the law is that the total entropy change of the system and the surroundings put together *must be positive*. The entropy change for either the system or the surroundings may even be negative. Thus, for a spontaneous process if the entropy of the system decreases, the entropy of the surroundings increases even more so as to offset the decrease in system's entropy, such that the sum of their entropies is positive. For example, for spontaneous freezing of a liquid (or condensation of a gas) the entropy of the system decreases. However, this decrease in entropy is more than compensated by the increase in the entropy

of the surroundings. The total entropy change for the system and the surroundings becomes positive and these processes are spontaneous.

Thus, we have a criterion for spontaneity of a process in terms of its entropy change. However there is a limitation in applying this criterion to different systems. This is so because it requires calculating the entropy changes for the system as well as for the surroundings. Calculation of the entropy change for the system is relatively straightforward, but it is quite tedious (sometimes not practical) to calculate the entropy change for the surroundings. Therefore, we need a criterion for spontaneity that depends only on the properties of the ‘system’. We would introduce such a criterion in the next section. For now let us share different statements of the Second Law of thermodynamics. These statements are equivalent; though these may not appear to have much connection with each other. The significant statements of the Second Law of thermodynamics and their authors are as under.

### Clausius (1850)

*“Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time”*. In simple words, “it is impossible to transfer heat from a colder body to hotter body without doing some work.”

### Kelvin (1851)

It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.

### Planck

It is impossible to construct an engine, which will work in a complete cycle, and produce no effect except the raising of a weight and cooling of a heat reservoir.

### Lewis

“In any irreversible process the total entropy of all the bodies concerned (system and surroundings) is increased.”

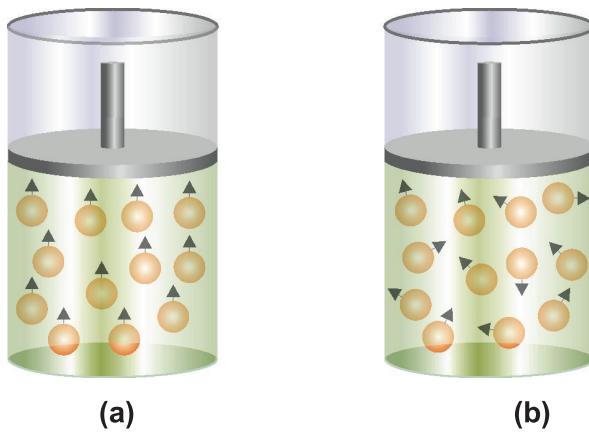
### Kelvin-Plank

“The thermal efficiency of a cyclic heat engine must be less than one, or less than 100 percent.”

When we say that the efficiency of a heat engine can never be hundred per cent it means that no heat engine can completely convert heat into work in a cyclic process even if the process is reversible. As you have learnt above that all real processes are irreversible therefore, their efficiency is even lesser than that of a reversible engine.

In case of a reversible engine the entire amount of heat absorbed is converted into kinetic energy of gas molecules and they start moving faster. If all the heat absorbed had to be converted to work (i.e., 100 % efficiency) then it would be necessary that all the molecules of the gas move in the same direction

simultaneously and hit the piston of the engine perpendicularly as shown in Fig 4.4 (a). This you know is highly improbable because the molecules are in random motion. Thus, only a certain fraction of them would hit the piston and push it Fig. 4.4 (b), and the efficiency would be less than 100%.



**Fig. 4.4:** (a) All the molecules of the gas need to simultaneously strike the piston in same direction to completely convert heat into work b) In real systems due to random motion of the molecules only a fraction of the molecules hit the piston and efficiency is less than 100%.

## 4.4 THE GIBBS ENERGY

$$q_{\text{sur}} = -q_{\text{sys}}$$

As the surroundings are big in size, therefore the transfer of heat from the surroundings can be considered as a reversible process.

$$q_{\text{sur}} = -q_{\text{rev(sys)}}$$

at constant pressure

$$q_{\text{rev(sys)}} = \Delta H_{\text{sys}}$$

$$q_{\text{sur}} = -q_{\text{sys}} = -\Delta H_{\text{sys}}$$

$$\Delta S_{\text{sur}} = \frac{-q_{\text{sys}}}{T} = \frac{-\Delta H_{\text{sys}}}{T}$$

As stated above, we need a criterion for spontaneity that depends on the properties of the system only. Such a criterion is 'Gibbs energy'. Let us learn about Gibbs energy and its significance. From Eq. (4.53) we can write that for a spontaneous process,

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

For a process at constant pressure, we can substitute  $\Delta S_{\text{surr}}$  by  $-\frac{\Delta H_{\text{sys}}}{T}$

$$\Rightarrow \Delta S_{\text{total}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \quad \dots(4.54)$$

On multiplying the Eq. (4.54) throughout by  $T$  we get

$$T \Delta S_{\text{total}} = T \Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0 \quad \dots(4.55)$$

This provides us a criterion for spontaneity in terms of the properties of system only.

Now if we multiply Eq. (4.55) by  $(-1)$  throughout, we get

$$-T \Delta S_{\text{total}} = -T \Delta S_{\text{sys}} + \Delta H_{\text{sys}} < 0 \quad \dots(4.56)$$

You may note here that the greater than sign in Eq. (4.55) is changed to less than sign on multiplying by  $(-1)$ . On rearranging Eq. (4.56) we get,

$$\Delta H_{\text{sys}} - T \Delta S_{\text{sys}} < 0 \quad \dots(4.57)$$

This implies that for a thermodynamic process carried at constant pressure ( $p$ ) and temperature ( $T$ ), if the changes in enthalpy and entropy of the system are such that  $\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$  then the process must be spontaneous. As this expression involves three properties of the system and gives a condition for spontaneity it prompts us to define a new thermodynamic property called Gibbs energy ( $G$ ) as

$$G = H - TS \quad \dots(4.58)$$

Gibbs energy (earlier called as Gibbs free energy) is denoted by the symbol  $G$  and like  $U$ ,  $H$  and  $S$  is a state function. We cannot determine its absolute value; however we can determine the change in Gibbs energy for a system and this acts as the criterion for spontaneity. Gibbs energy is an extensive property and the Gibbs energy per mole i.e., molar Gibbs energy ( $G_m$ ) is an intensive property. The SI unit for Gibbs energy is joule (J) and that of molar Gibbs energy, joule per mole ( $J \text{ mol}^{-1}$ ). Thus, the condition for spontaneity is that  $\Delta G < 0$ , i.e., the change in Gibbs energy should be negative for a process to be spontaneous.

At constant temperature and pressure, the chemical reactions are spontaneous in the direction in which the Gibbs energy decreases.

### Significance of Gibbs energy

We have defined Gibbs energy as

$$G = H - TS \quad \dots(4.58)$$

We know that,  $H = U + pV$

Therefore, we can write

$$G = U + pV - TS \quad \dots(4.59)$$

For an infinitesimal change, the equation becomes

$$dG = dU + pdV + Vdp - TdS - SdT \quad \dots(4.60)$$

From the First Law of thermodynamics

$$dU = dq + dw \quad \dots(2.6)$$

For a reversible process, we can write by rearranging Eq. (4.8)

$$dq_{\text{rev}} = TdS \quad \dots(4.61)$$

Also,  $dw = dw_{\text{rev}}$

$$\Rightarrow dU = TdS + dw_{\text{rev}} \quad \dots(4.62)$$

Substituting in Eq. (4.60)

$$\Rightarrow dG = TdS + dw_{\text{rev}} + pdV + Vdp - TdS - SdT \quad \dots(4.63)$$

Simplifying,

$$\Rightarrow dG = dw_{\text{rev}} + pdV + Vdp - SdT \quad \dots(4.64)$$

Under the conditions of constant  $T$  and  $p$  ( $dT = 0$  and  $dp = 0$ ), the expression becomes

$$dG_{p,T} = dw_{\text{rev}} + pdV = dw_{\text{rev}} - (-pdV) \quad \dots(4.65)$$

At constant pressure and temperature,  $dG$  represents non mechanical work.

On the right side of the Eq. (4.65) the first term ( $dw_{rev}$ ) represents all types of work in the process whereas the second term ( $-pdV$ ) is for the mechanical work. In other words we can say that  $dG_{p,T}$  represents the non-mechanical work. This expression finds application in assessing the electrical work produced by fuel cells and electrochemical cells.

### Properties of Gibbs energy

Once again from Eq. (4.60)

$$dG = dU + pdV + Vdp - TdS - SdT \quad \dots(4.60)$$

For a closed system doing only work of expansion, we can write Eq. (4.62) as

$$\rightarrow dU = TdS - pdV \quad \dots(4.66)$$

Substituting in Eq. (4.60), we get

$$dG = TdS - pdV + pdV + Vdp - TdS - SdT \quad \dots(4.67)$$

On simplification we get an important equation

$$dG = Vdp - SdT \quad \dots(4.68)$$

This implies that for a system with constant composition  $G$  is a function of  $p$  and  $T$  i.e.,  $[G = f(p, T)]$

Therefore, we can write total differential of  $G$  as

$$dG = \left( \frac{\partial G}{\partial p} \right)_T dp + \left( \frac{\partial G}{\partial T} \right)_p dT \quad \dots(4.69)$$

The terms in the brackets on right hand side of Eq. (4.69) represent the partial differentials where we take derivative of the property w.r.t one variable while keeping the other variable constant. The first term on right hand side in the Eq. (4.69) represents the rate at which the Gibbs energy changes with pressure at constant temperature multiplied by the change in pressure. Similarly, the second term represents the rate at which the Gibbs energy changes with temperature at constant pressure multiplied by the change in temperature.

Comparing Eq. (4.68) and Eq. (4.69) we get

$$\left( \frac{\partial G}{\partial p} \right)_T = V \quad \dots(4.70)$$

$$\left( \frac{\partial G}{\partial T} \right)_p = -S \quad \dots(4.71)$$

These are very important relations. According to Eq. (4.70) for a system with constant composition increase in pressure increases Gibbs energy (as  $V > 0$ ) and according to Eq. (4.71) for a system with constant composition increase in temperature decreases Gibbs energy (as  $S > 0$ )

## Enthalpy and Entropy driven reactions

You would recall that while discussing about decrease in enthalpy as a criterion for spontaneity we found that there are a number of examples of reaction accompanied by an increase in enthalpy ( $\Delta H > 0$ , endothermic process). Therefore, decrease in enthalpy could not serve as the desired criterion. Let's revisit spontaneous endothermic reactions in terms of Gibbs energy change. In such reactions  $\Delta H > 0$  but for spontaneity  $\Delta G$  must be negative. This is possible only when the entropy change for the system is positive (increases) and secondly it is so much positive that  $T\Delta S$  term in the expression;  $\Delta G = \Delta H - T\Delta S$  is greater than the  $\Delta H$  term. Such reaction are said to be '**entropy driven**' reactions because in such cases the decrease in Gibbs energy is caused by the entropy term.

Similarly, if for a reaction  $\Delta H$  as well as  $\Delta S$  were negative then the value of  $\Delta G$  would depend on the relative magnitude of  $\Delta H$  and  $-T\Delta S$  terms. The value of  $\Delta G$  would be negative only if  $\Delta H$  is highly negative such that it outweighs the  $-T\Delta S$  term (which is positive). Since in such a case the Gibbs energy decrease is due to the decrease in enthalpy of the system; such reactions are called **enthalpy driven** reactions.

### Chemical potential

For a chemical system with variable composition Gibbs energy is a function of the temperature, pressure and the composition i.e., the number of moles of different components;  $[G = f(p, T, n_1, n_2, n_3, \dots, n_i)]$

Therefore, we can write total differential of  $G$  as

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T, n_i} dp + \left(\frac{\partial G}{\partial T}\right)_{p, n_i} dT + \sum \left(\frac{\partial G}{\partial n_i}\right)_{T, p, n_j} dn_i \quad \dots(4.72)$$

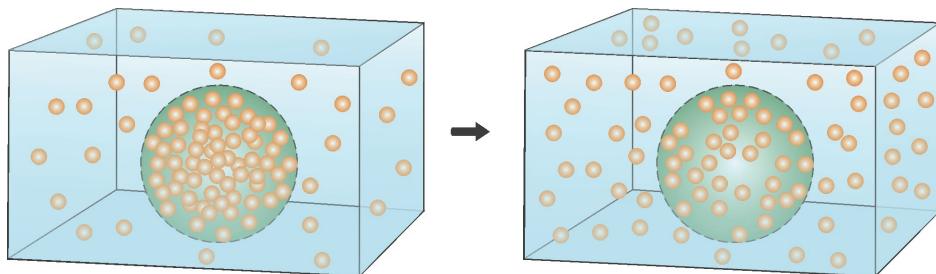
The first and second terms are similar to the ones described for Eq. (4.69). The third term in Eq. (4.72) gives the sum of partial derivatives of  $G$ , w.r.t to different components ( $i=1, 2, 3, \dots$ ) when  $T, P$ , and the number of moles of other components is held constant multiplied by the total change in number of moles of component  $i$ . This term for a given component (say  $i$ ) is an important property called chemical potential ( $\mu_i$ ) and is defined as

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, p, n_j} \quad \dots(4.73)$$

A detailed account of the chemical potential is beyond the scope of this course. However, we can state that chemical potential can be seen as 'escaping tendency' of a substance in a mixture. The molecules of a component spontaneously move from regions of high chemical potential to the regions of low chemical potential in a mixture. This continues till the chemical potential of the component becomes same throughout the system. For example, if we add a drop of ink in some water taken in a beaker then the molecules of ink in the region of drop gradually but spontaneously spread out. There is a concentration gradient and the molecules at higher chemical potential move spontaneously to the regions of low chemical potential i.e., they

Chemical potential is the rate of change of Gibbs energy with the number of moles of component  $i$  when the temperature, pressure and the number of moles of other components is kept constant.

diffuse. Fig. (4.5) gives a schematic representation of a concentration gradient. The species inside the porous membrane (at higher chemical potential) diffuse out to the region of lower chemical potential outside the membrane.



**Fig. 4.5: Schematic representation of a concentration gradient.**

Having learnt about Gibbs energy and its importance in predicting the spontaneity of a reaction let's now move to the Third Law of Thermodynamics. However, before moving to the Third Law solve the following simple question.

### SAQ 5

Crystallisation of a supersaturated solution of sodium acetate is spontaneous and exothermic process. Is the process 'entropy driven' or 'enthalpy driven'? Justify your answer.

## 4.5 THE THIRD LAW OF THERMODYNAMICS

So far we have introduced four state functions, viz., internal energy, enthalpy, entropy and Gibbs energy. You know that the value of state functions for a given system depend on the state and are independent of the path by which the state is achieved. Also we have learnt that we cannot measure the absolute value of a given state function in a given state but can measure the change in the state function for the process. This is so because we do not have a reference point (so called zero). However of these state functions, entropy is different from rest because we can, in principle, determine or estimate the absolute entropy of a system. This is made possible by the Third Law of thermodynamics that provides the 'zero' of the entropy scale. Let's try to understand it.

You know that a substance in gaseous state has greater entropy than that in the liquid state because in gaseous state there is a greater degree of disorder. Liquid state in turn has greater entropy than that of the solid state for the same reason. Further, as you know that when a solid is formed the constituent species pack closely in the lattice. Though the particles do not change their positions they vibrate about their mean positions. Now, if we start cooling a solid the motion of the species would be decreased and at 0 K it would stop completely. In this state since there is no disorder even due to the vibration of particles there would be perfect order so the entropy would be zero. (You know that entropy is a measure of disorder). This fact is stated as the Third Law of thermodynamics, which states that, "***the entropy of a pure and perfect crystalline solid at 0 K is zero.***"

This is in agreement with the statistical view of entropy also in which the entropy is related to the number of microstates; the greater the number of microstates, the larger is the entropy of the system. As in a pure and perfect crystalline solid there can be only one way to arrange constituents. This means that there is only one microstate possible which in turn means that the entropy ( $S = k \ln W = k \ln 1 = 0$ ) is equal to zero.

You have so far learnt about three laws of thermodynamics. Of these, the first and second laws are universally applicable to all types of substances whether they are pure or are mixtures and may be in any physical state. However, the Third Law is different as it is applicable only to substances in solid state and more so they have to be pure and perfectly crystalline in nature. The Third Law is different in a yet another way as contrary to the First and Second Laws; the Third Law has an exception. It has been found that for certain substances the entropy does not become zero even at 0 K. The entropy of a crystalline substance at 0 K temperature is known as residual entropy about which you would learn a little later. Let's first learn how to calculate absolute entropies of substances.

#### 4.5.1 Determination of Absolute Entropy

Once we have defined the 'zero' of the entropy scale it becomes possible to determine the absolute entropy of a substance under a given set of conditions of temperature and pressure. We have seen that at 0 K there is only one possible microstate. If we increase the temperature the freedom of motion of the constituent species increases and so do the number of microstates. This means that the entropy of any substance at a temperature above 0 K is greater than zero and is called its **absolute entropy**. Suppose we heat a pure and perfect crystalline solid at 0 K to a temperature of say 10 K and measure the entropy change for the process it would be

$$\Delta S = S_{10\text{K}} - S_{0\text{K}} = S_{10\text{K}} - 0 = S_{10\text{K}} \quad \dots(4.74)$$

You must remember that it is not possible to define a 'zero' for internal energy, enthalpy and Gibbs energy so we cannot determine their absolute values.

Thus, the entropy change would provide the absolute entropy of the substance at 10 K. Similarly, we can determine the absolute entropies at any set of temperature and pressure conditions. For this we need to consider different changes occurring in the system as we heat it from 0 K onwards. As we heat the solid at 0 K onwards its entropy would continue to increase till it reaches its melting point. At the melting point there would be a sharp increase in the entropy due to the phase change from solid to liquid. Then on further heating the entropy would continue to increase as the kinetic energy of the molecules of liquid increases leading to more disorder or randomness. Once again, there would be a sharp increase in the entropy at the next phase change from liquid to the vapour phase at the boiling point. Here, the increase in entropy would be much larger than that observed in the phase transition from solid to liquid. In addition to these changes if the substance undergoes some other phase change say from a given crystalline form to the other one there would be corresponding changes in the entropy.

The expression given in Eq. (4.74) is quite simplistic. In order to calculate the absolute entropy of a substance at a given temperature and pressure we can derive the expression as follows.

From Eq. (4.8) we know that

$$dS = \frac{dq_{rev}}{T} \quad \dots(4.8)$$

We can write from Eq. (2.45)

$$dq_p = C_p dT \quad \dots(2.45)$$

Substituting in Eq. (4.8)

$$dS = \frac{C_p dT}{T} \quad \dots(4.75)$$

To get the value of absolute entropy we need to integrate Eq. (4.75) in the limits of 0 to  $T$  K, where the entropy changes from 0 to  $S$  we get

$$\int_0^S dS = \int_0^T C_p \frac{dT}{T} \quad \dots(4.76)$$

Thus, we can calculate the absolute entropy of a substance at temperature  $T$  if we know the heat capacity of the solid in the temperature range of 0 K to  $T$  K. However, there is a problem that the heat capacities cannot be determined at temperature close to  $T = 0$  K. The heat capacities have been measured to as low a temperature as about 10 K but for temperatures below that we need to depend on empirical expression given by Debye, according to which the heat capacity of a non-metallic solid is proportional to  $T^3$  ( $C_p = aT^3$ ) where  $T$  is the temperature at which the entropy value is required. Thus, the expression for computing the entropy of a substance at a temperature  $T$  close to 0 K can be given as follows.

$$\int_0^S dS = \int_0^T aT^3 \frac{dT}{T} \quad \dots(4.77)$$

as 'a' is a constant we can take it out of the integral and write

$$\int_0^S dS = a \int_0^T T^2 dT \quad \dots(4.78)$$

On integrating, we get

$$[S]_0^T = a \left[ \frac{T^3}{3} \right]_0^T \quad \dots(4.79)$$

On simplification,

$$S(T) - S(0) = \frac{a}{3} T^3 \quad \dots(4.80)$$

$$S(T) = S(0) + \frac{a}{3} T^3 \quad \dots(4.81)$$

$$S(T) = S(0) + \frac{1}{3} C_{p,m}(T) \quad \dots(4.82)$$

This expression can be used to calculate the absolute entropy of a substance at very low temperatures. However, if we wish to calculate the absolute entropy of a substance above the minimum temperature at which entropy can be measured then we need to add more terms. For example if we want to calculate the entropy at a temperature greater than its melting point ( $T_f$ ) then the expression becomes as follows.

$$\int_0^S dS = a \int_0^{T_m} T^2 dT + \int_{T_m}^{T_f} C_p(s) \frac{dT}{T} + \frac{\Delta_f H}{T_f} + \int_{T_f}^T C_p(l) \frac{dT}{T} \quad \dots(4.83)$$

The first term is for the entropy change upto the minimum temperature ( $T_m$ ) at which the heat capacity can be determined. The second term is for the entropy change from  $T_m$  to  $T_f$ . The third term gives the contribution of the phase transition whereas the last term is for the increase in entropy of the liquid from melting point to the temperature of interest. If the temperature of interest happens to be more than the boiling point of the substance then the equation would get further modified. We would need to incorporate another phase change and so on. The desired expression for the calculation of absolute entropy of a substance at a temperature above its boiling point would be

$$\int_0^S dS = a \int_0^{T_m} T^2 dT + \int_{T_m}^{T_f} C_p(s) \frac{dT}{T} + \frac{\Delta_f H}{T_f} + \int_{T_f}^{T_b} C_p(l) \frac{dT}{T} + \frac{\Delta_{vap} H}{T_{vap}} + \int_{T_b}^T C_p(g) \frac{dT}{T} \dots(4.84)$$

It is important to note that the entropies calculate on the basis of third law statement,  $S(0)=0$ , are called as **third law entropies** or just entropies.

### 4.5.2 Residual Entropy

As mentioned above, the entropy of some pure and perfectly crystalline solids is found to be non-zero at 0 K and is called as residual entropy. The residual entropies of some substances are given in Table 4.1.

**Table 4.1: Residual entropies of some substances**

Substance	Molecular formula	Residual entropy / $\text{JK}^{-1} \text{mol}^{-1}$
Hydrogen	$\text{H}_2$	6.2
Carbon monoxide	CO	3.4
Ice	$\text{H}_2\text{O}$	5.8

You may note here, that the residual entropy is observed in substances containing molecules, which are either non-polar or have very small dipole moment. The residual entropy of  $3.4 \text{ J K}^{-1} \text{ mol}^{-1}$  at 0 K for diatomic carbon monoxide implies that the crystalline carbon monoxide does not have a perfect arrangement of the CO molecules. We can say that in the crystalline state its arrangements like, ..COCOCO..and ..OCCOCO..may not have significant difference in their energies. In other words more than one arrangement are possible for the molecules of carbon monoxide at 0 K, i.e., the number of microstates is more than 1 so the entropy is not zero. The residual entropies can be theoretically calculated using statistical thermodynamics. This is beyond the scope of this course.

Having learnt about the Third Law of thermodynamics, its significance and determination of absolute entropies answer the following simple question to assess your understanding.

### SAQ 6

Differentiate between the Third Law entropy and residual entropy of a system.

## 4.6 SUMMARY

In this last unit of the block we took up the Second and the Third Law of thermodynamics. We began the unit by initiating a discussion on spontaneity and need for a criterion for the same. In this process we examined different spontaneous and non-spontaneous processes and noted that if a physical or a chemical change is spontaneous in one direction, it is not spontaneous in the opposite direction. Secondly, both spontaneous and non-spontaneous processes are possible, but only spontaneous processes occur on their own; the non-spontaneous processes require the help of an external agent to occur. We then examined and showed that internal energy or enthalpy cannot serve as a criterion for spontaneity. In this light we argued for the need of a new thermodynamic parameter that could serve as a criterion for spontaneity.

Thereafter we introduced the concept of entropy as a measure of dispersal of energy and matter by analysing different processes and gave the thermodynamic definition of entropy. It is also a measure of disorder. It was pointed out that in order to calculate the entropy change for a process we need to use the transfer of heat to or from the system in a reversible way irrespective of the fact whether the process is reversible or irreversible. This in fact is a consequence of entropy being a state function. We then took up the statistical viewpoint on entropy according to which the entropy of the system depends on the number of possible ways of distributing the energy of the system. Each of these ways is called a microscopic state or a microstate. Further, each set of similar microstates is called a *distribution* or a *state*. The probability of a particular distribution depends on the number of microstates in it. Greater the number of microstates in a distribution greater is its entropy. We then derived expressions for calculating the entropy changes in some simple processes.

Having introduced the concept of entropy and learning about computing entropy changes in different processes we evaluated entropy as a criterion for spontaneity. We demonstrated that entropy does help in ascertaining whether a process will be spontaneous or not. For this it was shown that the total entropy change in an isolated system i.e., the entropy change for the system and the surroundings must increase for the process to be spontaneous. This in fact formed the basis of stating the Second Law of thermodynamics for which we gave a number of equivalent statements. However, entropy as a criterion for spontaneity is difficult to apply, as it requires calculation of entropy change for the system as well as for the surroundings. This prompted us to introduce Gibbs energy as a criterion for spontaneity as it depends on the properties of the system only. It was shown that for a process to be spontaneous the Gibbs energy must decrease. We then briefly discussed about enthalpy driven and entropy driven reactions.

Thereafter we introduced the Third Law of thermodynamics, which states that at a temperature of 0 K the entropy of a pure and perfect crystalline solid is 0. This provided the reference point for entropy and was used to calculate the absolute entropy of a substance at a given temperature. During the discussion on the Third Law of thermodynamics we introduced the concept of residual entropy as the non-zero entropy of certain substances at 0 K. This in fact is an exception to the Law.

## 4.7 TERMINAL QUESTIONS

1. The molar enthalpy of fusion of a monoatomic noble gas is found to be  $1.3 \text{ kJ mol}^{-1}$ . If the melting point of the gas is  $-190^\circ\text{C}$  calculate the molar entropy of fusion for the gas.
2. 1 mole of argon at 298 K and 1.00 bar taken in a container is confined to a volume of  $5.00 \text{ dm}^3$ . In a composite process the gas is allowed to expand to double its initial volume and is simultaneously heated to reach a temperature of 323 K. Calculate the entropy change for the process assuming ideal gas behaviour. [Given  $C_{v,m}=12.47 \text{ J K}^{-1} \text{ mol}^{-1}$ ].
3. According to Kelvin-Planck statement of the Second Law of thermodynamics, the efficiency of a heat engine cannot be 100%. Justify the statement.
4. Explain enthalpy driven and entropy driven reactions. Melting of ice is an endothermic process. Is the process 'entropy driven' or 'enthalpy driven'? Justify your answer.
5. Define chemical potential and explain its significance.

## 4.8 ANSWERS

### Self-Assessment Questions

1. Spontaneous reactions are the reactions that occur on their own under a given set of conditions without the aid of any external agency. No, the internal energy cannot serve as a criterion for spontaneity of a chemical reaction.
2. i) Decrease    ii) Decrease    iii) Increase    iv) Increase
3. The entropy of mixing of  $n_A$  moles of gas A occupying a volume  $V_A$  with  $n_B$  moles of gas B occupying a volume  $V_B$  is given by the following expression

$$\Delta S_{mixing} = 2.303 R \left[ n_A \log \frac{V_A + V_B}{V_A} + n_B \log \frac{V_A + V_B}{V_B} \right]$$

In the present case the given data is as under

$$n_A = 1.00 \text{ mol} \quad n_B = 1.00 \text{ mol} \quad V_A = 5 \text{ dm}^3 \quad V_B = 10 \text{ dm}^3$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

Substituting the values in the equation, we get

$$\Delta S_{mixing} = 2.303 \times 8.314 \text{ J K}^{-1}\text{mol}^{-1} \left[ 1.0\text{mol} \times \log \frac{5+10}{5} + 1.0\text{mol} \log \frac{5+10}{10} \right]$$

Simplifying and solving

$$\Delta S_{mixing} = 2.303 \times 8.314 \text{ J K}^{-1} [\log(3.0) + \log(1.5)] = 19.147 \log(4.5) \text{ J K}^{-1}$$

$$\Delta S_{mixing} = 12.51 \text{ J K}^{-1}$$

4. The entropy change for fusion of a liquid is given by Eq. (4.39)

$$\Delta_f S = \frac{\Delta_f H}{T_f}$$

We are provided with the enthalpy and the temperature of fusion.

Substituting the values in the expression, we get

$$\Delta_f S = \frac{-6.02 \text{ kJ mol}^{-1}}{273.1 \text{ K}} = \frac{-602 \text{ J mol}^{-1}}{273.1 \text{ K}} = -2.204 \text{ J K}^{-1}\text{mol}^{-1}$$

5. The process is enthalpy driven. This is so because the crystallisation process is accompanied by a decrease in entropy i.e.,  $\Delta S$  is negative which means  $-T\Delta S$  term is positive. On the other hand the enthalpy change is negative (exothermic). We know that

$$\Delta G = \Delta H - T\Delta S = \Delta H + (-T\Delta S)$$

The first term ( $\Delta H$ ) is negative and the second term ( $-T\Delta S$ ) is positive. As a consequence the change in Gibbs energy can be negative only if the enthalpy change is highly negative so that the sum of two terms becomes negative. As the factor contributing towards making Gibbs energy change negative is the enthalpy change so we say that the process is enthalpy driven.

6. The third law entropy refers to the entropy of a substance at a given temperature w.r.t its entropy in pure and perfect crystalline state at 0 K to be equal to zero. On the other hand, the residual entropy refers to the entropy of a substance at absolute zero (0 K). This is due to imperfections in the crystal at 0 K.

## **Terminal Questions**

1. The entropy change for fusion of a liquid is given by Eq. (4.39)

$$\Delta_f S = \frac{\Delta_f H}{T_f}$$

We are provided with the enthalpy and the temperature of fusion for the substance. Substituting the values in the expression, we get

$$\Delta_f S = \frac{-1.3 \text{ kJ mol}^{-1}}{83 \text{ K}} = \frac{-1300 \text{ J mol}^{-1}}{83 \text{ K}} = -15.66 \text{ J K}^{-1}\text{mol}^{-1}$$

2. The process can be written as

$$(5.0 \text{ dm}^3, 298 \text{ K}) \rightarrow (10.0 \text{ dm}^3, 323 \text{ K})$$

In this process the temperature as well as the volume of the system is changing. Now, since entropy is a state function, the entropy change would remain same irrespective of the path chosen. So for convenience we break this composite process into two steps process as follows.

$$(5.0 \text{ dm}^3, 298 \text{ K}) \rightarrow (10.0 \text{ dm}^3, 298 \text{ K}) \rightarrow (10.0 \text{ dm}^3, 323 \text{ K})$$

This means that in the first step the gas undergoes isothermal reversible expansion and in the second step the gas is reversibly heated at constant volume. The entropy change for the first step can be calculated by using Eq. (4.19) i.e.,

$$\Rightarrow \Delta S_I = 2.303 nR \log \frac{V_2}{V_1}$$

We are given  $n = 1 \text{ mol}$      $V_1 = 5 \text{ dm}^3$  ;     $V_2 = 10 \text{ dm}^3$

Substituting the values in the equation, we get

$$\Rightarrow \Delta S_I = 2.303 \times 1.0 \text{ mol} \times (8.314 \text{ JK}^{-1}\text{mol}^{-1}) \log \frac{10}{5}$$

Solving, we get

$$\Rightarrow \Delta S_I = 5.76 \text{ J K}^{-1}$$

Stage 2: For the reversible heating of the gas at constant volume the entropy change can be calculated by using Eq. (4.34)

$$\Delta S_{II} = 2.303 C_{V,m} \log \frac{T_2}{T_1}$$

We are given:

$$C_{V,m} = 12.47 \text{ J K}^{-1}\text{mol}^{-1}; \quad T_1 = 298 \text{ K}; \quad T_2 = 323 \text{ K}$$

Substituting the values in the expression, we get

$$\Delta S_{II} = 2.303(12.47 \text{ J K}^{-1} \text{ mol}^{-1}) \log \frac{323}{298}$$

Solving, we get

$$\Delta S_{II} = 1.005 \text{ J K}^{-1}\text{mol}^{-1}$$

Total entropy change for the overall process would be

$$\Rightarrow \Delta S_I + \Delta S_{II} = 5.76 \text{ JK}^{-1}\text{mol}^{-1} + 1.005 \text{ JK}^{-1}\text{mol}^{-1} = 6.765 \text{ JK}^{-1}\text{mol}^{-1}$$

3. It is true that the efficiency of a heat engine cannot be 100 %. It is so because for the efficiency to be 100% all the heat absorbed by the gas should be converted to work. This is possible only if all the gas molecules that absorb heat must simultaneously push the piston while moving in same direction. However, as we know the molecules are in random motion and it is improbable that they push the piston simultaneously in the same direction. Only a few molecules will push the piston in the desired direction and hence the efficiency would be less than 100%.
4. We know that for a reaction to be spontaneous, the Gibbs energy change ( $\Delta G$ ) for the same should be negative. We also know that there are two contributors to the Gibbs energy change ( $\Delta G = \Delta H - T\Delta S$ ) i.e., the enthalpy change ( $\Delta H$ ) and entropy change (as  $T\Delta S$ ). These two factors can work in the same direction or in opposite direction. Accordingly, the Gibbs energy may increase or decrease as a resultant of the two. The process for which the enthalpy change is the main component in making Gibbs energy change negative is called enthalpy driven. In case this job is performed by entropy component then the process is referred to as entropy driven.

The given process is entropy driven. This is so because the melting of ice is accompanied by an increase in entropy i.e.,  $\Delta S$  is positive which means  $-T\Delta S$  term is negative. On the other hand, the enthalpy change is positive, as the process is endothermic. We know that

$$\Delta G = \Delta H - T\Delta S = \Delta H + (-T\Delta S)$$

The first term ( $\Delta H$ ) is positive and the second term is negative and large. As a consequence the change in Gibbs energy is negative and the factor contributing for this is the entropy change. Therefore the process is called as entropy driven.

5. The chemical potential is an important thermodynamic parameter and refers to the change in Gibbs energy of a system w.r.t the number of moles of one of its constituents of the system under the conditions of constant temperature, pressure and the number of moles of all other components. Mathematically,

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_j}$$

As regards the significance the chemical potential can be seen as 'escaping tendency' of a substance in a mixture. Molecules move spontaneously from regions of high chemical potential to regions of low chemical potential in a mixture till the chemical potential of the component becomes same throughout the chemical system.